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A review of potential materials for thermal energy storage in building applications

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ABSTRACT

In recent years, storage of thermal energy has become a very important topic in many engineering applications and has been the subject of a great deal of research activity. This paper reviews the thermal energy storage technologies suitable for building applications with a particular interest in heat storage materials. The paper provides an insight into recent developments on materials, their classification, their limitations and possible improvements for their use in buildings. Three major thermal energy storage modes (sensible heat, latent heat, thermochemical heat) are described emphasizing the main characteristics of the most suitable heat storage materials for each.

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Nomenclature

m	material mass (kg)
C_p	specific heat (J/(kg K))
k	thermal conductivity (W/(m K))
e	effusivity (W s$^{1/2}$/(m^2 K))
P	pressure (Pa)
Q	energy (J)
T	temperature (K)

Greek symbols

ρ	density (kg/m^3)
α	thermal diffusivity (m^2/s)

Subscripts

i	initial
f	final
0	reference

1. Introduction

In 2010, the building sector accounted for 25% of the total final energy consumption in the world, the third largest after industry (32%) and transport (31%) [1]. Although this share is expected to decrease, buildings will still account for 20% of the total final energy demand in the coming years. Space heating and domestic hot water production are key applications in this sector: 53% and 16%, respectively [1]. The prospect of an increasing scarcity of fossil fuel and the upward trend of oil prices have led to a general interest in renewable energy resources that are more respectful of the environment. Solar energy is one of them. This resource is abundant and offers unrestricted access. Considering building applications, solar energy has been used for space heating/cooling as well as hot water and electricity production for many years. Unfortunately, solar energy is intermittent and there is a mismatch between the supply and demand periods. The peak of the solar irradiation occurs during the day when the heating demand is low, and the highest demand usually occurs at night or early in the morning, when sun irradiation is low.

Consequently, there is a need for heat storage so that the excess heat produced during supply periods can be stored for use during peak demand periods. To this end, one of the most widely used techniques for thermal energy storage is the sensible heat storage method. The concept is widely used, well known, and is the simplest and least expensive way to store energy [2–4]. In addition, other energy storage techniques such as latent energy storage and thermochemical energy storage appear to be promising given their great heat storage capacity and/or their low heat losses during the storage period.

For all the energy storage methods mentioned above, their performance is strongly dependent on the nature of the storage material chosen in the system. A material with a high heat storage capacity and good heat transfer characteristics will improve the performance of the heat storage system. Some other material parameters such as the cost, environmental impact, and safety conditions, also play an important role and therefore should be taken into account during the design of such systems.

The aim of this paper is to present a review of materials available for thermal energy storage in buildings. The temperatures concerned range from 0 to 100 °C. Indeed, building heat consumption covers both cooling (for air conditioning) and heating purposes (for space heating and domestic hot water production). Domestic food refrigeration and freezing will not be considered in this paper. Heat storage methods will be introduced with an emphasis on the thermophysical properties of the material used. One of the key properties is the energy density of the storage materials. In buildings, given that space is a critical feature, the volumetric energy density will be considered.

2. Sensible heat storage

One definition of sensible heat storage materials is that of materials that are not subject to a phase change during the temperature change of the heat storage process [5]. The amount of energy involved in a sensible heat storage process depends, as presented in Eq. (1), on the specific heat of the material ($C_p(T)$), the temperature change (T_f,T_i), and the amount (m) of material.

$$Q = \int_{T_i}^{T_f} mC_p(T)dT \tag{1}$$

It is important for sensible heat storage systems to use a heat storage material that has high specific heat capacity in addition to good thermal conductivity, long-term stability under thermal cycling, compatibility with its containment, recyclability, a low CO_2 footprint, and most important, low cost. Moreover, for building applications, high density is also essential. Various disadvantages are inherent to sensible heat storage systems. The most important of them are: their relatively low energy density (space limitation is usually a critical aspect, especially for building applications) and the system's self-discharge (heat losses), which can be substantial, particularly when long periods of storage are needed.

Sensible heat storage materials have been widely investigated. Most authors present these materials in two main groups: liquid and solid storage mediums. Liquids are most often water and thermal oil, and solids are rocks, bricks, concrete, iron, dry and wet earth, and many others.

2.1. Liquid storage materials

Table 1 shows a list of liquid materials used in sensible heat storage systems. These materials can be classified according to their operating temperature. Water has been widely used for heat storage as well as for heat transport purposes in energy systems.

Table 1
List of selected solid and liquid materials for sensible heat storage in building applications.

Material	Type	Temperature range (°C)	ρ (kg/m^3)	C_p (kJ/(kg K))	k (W/(m K)) (at 20 °C)	e (W s$^{1/2}$/(m^2 K))	References
Water	Liquid	0–100	1000	4.19	0.58	49.30	[188]
Caloriea HT43	Liquid	12–260	867	2.2	–	–	[189]
Ethanol	Liquid	Up to 78	790	2.4	0.171	18.01	[188]
Proponal	Liquid	Up to 97	800	2.5	0.161	17.94	[188]
Butanol	Liquid	Up to 118	809	2.4	0.167	18.01	[188]
Isobutanol	Liquid	Up to 100	808	3	0.133	17.96	[188]
Isopentanol	Liquid	Up to 148	831	2.2	0.141	16.06	[188]
Octane	Liquid	Up to 126	704	2.4	0.134	15.05	[190]
Engine Oil	Liquid	Up to 160	888	1.88	–	–	[188]
Brick	Solid	20–70	1600	0.84	1.20	1270	[188]
Concrete	Solid	20–70	2240	1.13	0.9–1.3	47.73–57.36	[189]
Cement sheet	Solid	20–70	700	1.050	0.36	514	[29]
Gypsum plastering	Solid	–	1200	0.837	0.42	649	[29]
Granite	Solid	20–70	2650	0.900	2.90	2967	[29,191]
Marble	Solid	20–70	2500	0.880	2.00	2285	[29,192]
Sandstone	Solid	20–70	2200	0.712	1.83	1710	[29,192]
Clay sheet	Solid	–	1900	0.837	0.85	1163	[29]
Asphalt sheet	Solid	–	2300	1.700	1.20	2166	[29]
Steel slab	Solid	20–70	7800	0.502	50	13,992	[29]
Cork board	Solid	–	160	1.888	0.04	110	[29,191]
Wood	Solid	–	800	2.093	0.16	324	[29,191]
Plastic board	Solid	–	1050	0.837	0.50	663	[29]
Rubber board	Solid	–	1600	0.200	0.30	310	[29]
PVC board	Solid	–	1379	1.004	0.16	410	[29,192]
Asbestos sheet	Solid	–	2500	1.050	0.16	648	[29]
Formaldehyde board	Solid	–	30	1.674	0.03	39	[29]
Thermalite board	Solid	–	753	0.837	0.19	346	[29]
Fiber board	Solid	–	300	1	0.06	134	[29]
Siporex board	Solid	–	550	1.004	0.12	257	[29]
Polyurethane board	Solid	–	30	0.837	0.03	27	[29]
Light plaster	Solid	–	600	1	0.16	712	[192]
Dense plaster	Solid	–	1300	1	0.50	806	[29]
Aluminum	Solid	Up to 160	2707	0.896	204	703.42	[188]
Aluminum oxide	Solid	Up to 160	3900	0.84	30	313.50	[188]
Aluminumsulfate	Solid	Up to 160	2710	0.75	–	–	[189]
Cast iron	Solid	Up to 160	7900	0.837	29.3	440.16	[188]
Pure iron	Solid	Up to 160	7897	0.452	73	510.46	[189]
Calcium chloride	Solid	Up to 160	2510	0.67	–	–	[189]
Copper	Solid	Up to 160	8954	0.383	385	1149.05	[188]
Stone, granite	Solid	Up to 160	2640	0.82	1.7–3.98	61.20–92.82	[189]
Stone, sandstone	Solid	Up to 160	2200	0.71	1.83	53.46	[189]

(–): not available.

It appears to be the best of sensible heat storage liquids for temperatures lower than 100 °C because of its availability, its low cost, and, most important, its relatively high specific heat [6]. For a 70 °C temperature change (20–90 °C), water will store 290 MJ/m^3. Today, it is also the most widely used storage medium for solar-based warm water and space heating applications. A large amount of published data on the design criteria for systems with water as a heat storage material is available [2,7–9]. Water can be used in different storage techniques: storage tanks, aquifers, and solar ponds.

2.1.1. Water storage tanks

Water storage tanks are made of a wide variety of materials, such as steel, aluminum, reinforced concrete, and fiberglass. They generally have to be insulated with glass wool, mineral wool, or polyurethane to avoid thermal losses [10]. During the heat storage process, thermal stratification in a water heat storage tank can be established due to the buoyancy forces. This process makes it possible to have the highest temperature at the top and the lowest temperature at the bottom of the tank. The system's energy efficiency and performance are improved under these conditions. With stratification, the exergy (useful work potential content) efficiency of the system is also increased [10–13].

2.1.2. Aquifers

Aquifers are geological formations containing ground water [10]. Aquifer's water is sometimes mixed with gravel or sand. The main advantages of aquifers for heat/cold storage are the long storage periods allowed and their low overall cost due to the large volumes that can be stored [11].

Heat storage in aquifers consists in extracting ground water from a well, heating this water with an available heat source (solar collectors for instance), and then re-injecting it back into the aquifer in the other well, as illustrated in Fig. 1 [11]. The estimated heat storage capacity of 10^5 m^3 of aquifer is 3 MJ for each 10 K temperature range [10]. Because of its bulk nature, aquifer heat storage systems are considered to be best suited for large-scale storage applications such as centralized urban heating systems. Novo et al. [14] reviewed seasonal heat storage in large basins (water tanks and gravel–water pits). They found that energy costs can be reduced with increasing storage volume in large-scale solar applications. Compared to classical water storage tanks, this means that aquifer heat storage systems have lower investment and operational costs. In fact, use of the natural aquifer layer does not involve heavy excavation and the construction of a water tank, thus eliminating these costs. However, specific hydrogeological conditions are required for heat storage in aquifer sites [14,15]:

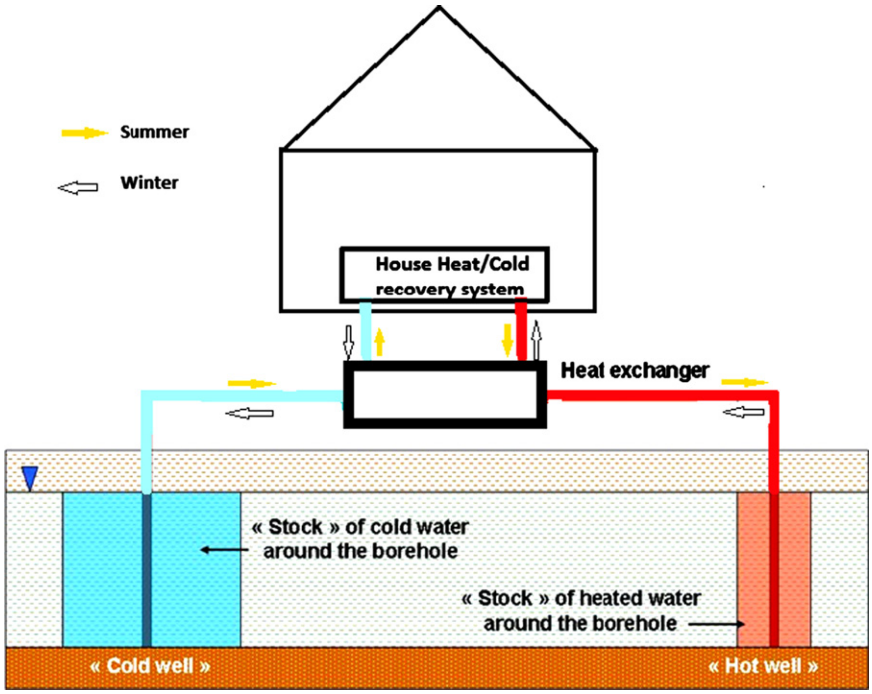


Fig. 1. Aquifer storage principle.

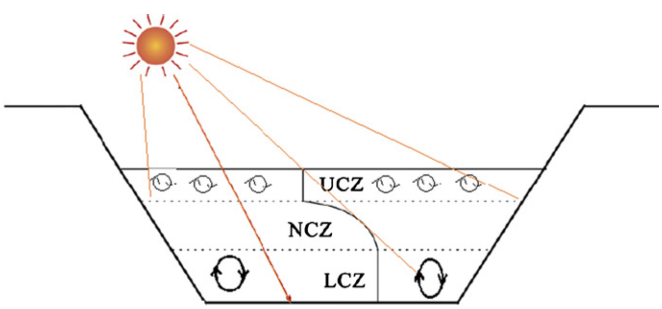


Fig. 2. Schematic of a solar pond (UCZ=Upper Convective Zone, NCZ=Non Convective Zone, LCZ=Lower Convective Zone).

- Natural aquifer layer with high conductivity;
- Confining layers above and below;
- No or low natural ground water flow;
- Suitable water properties at sufficiently high temperatures;
- Aquifer thickness 20–50 m.

Several experimental and theoretical studies provide more complete reviews of aquifers, their design, and their potential environmental impact [14,16–18].

2.1.3. Solar ponds/lakes

Solar ponds can be defined as large volumes of saline solution with a higher concentration of salts at the bottom than at the top. They are subdivided into three zones (Fig. 2): the upper convective zone (UCZ), which is located in the upper layers of the pond made up of low-salinity brine, the non convective zone (NCZ), which is located just below the UCZ and contains a salinity gradient such that the water at the top is always less salty than the water at the bottom of the pond, and the lower convective zone (LCZ), which has the greatest salinity density and where the heat is stored and extracted. Solar ponds offer an economical method for collecting and storing solar thermal energy in the temperature range 50–95 °C [10].

Solar ponds operate as follows: due to the salinity gradient within the pond, heat absorbed from solar irradiation remains trapped at the bottom. Indeed, the salinity gradient inhibits the natural convection within the pond and water at the surface remains cool and hence acts as an insulator for the deeper regions (Fig. 2) [19]. The heat stored can easily be removed with a heat exchanger system from the LCZ. Wang and Akbarzadeh [20] reported that solar ponds can provide a 20% efficiency (the ratio between the total energy extracted from the pond and its estimated energy capacity) for a heat recovery temperature not higher than 65 °C and a 15% efficiency with a heat recovery at 87 °C. Darkening the bottom of the pond results in more solar radiation being absorbed [19]. Heat extraction from a solar pond using heat pipes has been investigated by Andrews et al. [21]. According to the authors, maximum possible efficiency of solar pond systems with heat extraction only from the LCZ is limited to 30% [21]. However, this value can be enhanced by combining the extraction of heat from the LCZ to that of the NCZ. In this case, the pond's efficiency can be increased up to 50% [21].

The following conditions are required from suitable salts to be used in solar ponds [22]:

- A high value of solubility to allow high solution densities; also the solubility should not vary appreciably with temperature;
- Transparency of the salt solution to solar radiation;
- Environmentally benign and safe to handle;
- Low cost.

Solar ponds commonly use sodium chloride (NaCl), but some other salts such as natural brine (Na^+, K^+, Mg^{++},SO_2^-,Cl^-), magnesium chloride (MgCl), sodium carbonate (Na_2CO_3), potassium nitrate (KNO_3), ammonium nitrate (NH_4NO_3), and fertilizer salts such as urea ($NH_2CO \cdot NH_2$) have shown good thermal properties and stability and can also be used [23–26]. The best

efficiency is achieved with NaCl [23,24]. Hassairi et al. [23] compared two lakes of concentrated sodium chloride and natural brine. It appears that a higher temperature is reached with NaCl (with an average temperature at 55 °C) than with the natural brine. Kurt et al. [24] experimentally and theoretically investigated a solar pond saturated with sodium carbonate. The authors showed that having a temperature gradient within the pond required a salinity gradient (between the top and the bottom layers of the pond) higher than 12%.

2.2. Solid storage materials

Solid media are widely used for low as well as high-temperature storage. They usually consist of rocks, metals, concrete, sand, bricks, etc., as shown in Table 1. For building applications, solid materials are mostly used for space heating purposes. Their operating temperatures cover a wide range, from 40 to 70 °C for concrete or rocks, to over 160 °C for metals. The major drawback of using solids as heat storage materials is their low specific heat capacity (~1200 kJ/(m^3 K) on average), which results in a relatively low energy density (more than three times less energy stored than water in the same volume for the same temperature increase, for example). However, compared to liquid or gaseous materials, two main advantages are inherent to solid materials: their viability at high temperatures and no leakage problem with their containment [10]. The compatibility of the material with the heat transfer fluid used is of importance [6]. Also, the efficiency and the viability of heat storage systems with solid materials is strongly dependent on the solid material's size and shape, the packing density, the type of heat transfer fluid, the flow pattern, etc.

Solid metals appear to be suitable for high-temperature storage applications and where good heat conductivity is required. However, their relatively high cost limits their use. The materials most commonly in use in buildings for heat storage are those in the building structure and rocks.

2.2.1. Building structure

The building structure itself can be used as a medium for energy storage management. It plays a role as a thermal buffer to attenuate external heat flows and muffle internal temperature swings. It consists of using the building inertia as heat sink during the overheated periods and then recovering the stored heat when needed through an appropriate ventilation system [27] or by natural convection with the indoor air. The thermophysical properties of ordinary building envelope materials are listed in Table 1. It can be seen that building materials in general have low specific heat capacity and low heat conductivity, a major limitation for heat storage purposes. However, these materials have a relatively good density.

A number of recent studies have investigated the building's mass and components to minimize space heating costs [28,29]. Ståhl [28] conducted a detailed study on the thermal properties of building thermal inertia. He studied its influence on the overall efficiency and the heating demand. The author concluded that the main parameter is the thermal effusivity of the material. Greater thermal effusivity, which characterizes the rate at which a material can absorb heat, will result in a greater amount of heat stored and thus a decrease of the overall energy consumption of the building [28]. Based on this result, from materials listed in Table 1, brick, granite, marble, steel slabs or asphalt sheets have good potential in this context.

2.2.2. Rock beds

Energy storage systems with rocks consist of a bed of loosely packed rock material (rock beds) through which the heat transfer fluid (usually air) can flow. For building applications, this type of storage is often used in conjunction with solar collectors. During the charging phase, heated fluid flows from the solar collectors into the bed from top to bottom. When heat discharge is needed, the fluid flow is reversed.

Packed beds have been widely investigated both analytically and experimentally. Singh et al. [30] published a detailed review on packed bed solar energy storage systems with an emphasis on particle type and size as well as the range of parameters pertaining to the implementation of pebble beds for heat energy storage for buildings. Alkilani et al. [31] studied thermal storage units for solar air collectors and argued that a good heat transfer between air and solid particles enhances thermal stratification within the bed. Also, due to poor heat exchange by conduction between the rocks, the stratification can be maintained over considerable time periods. However, one limitation of the stratified rock bed systems is that they cannot be charged and discharged simultaneously. For the sizing of the storage vessel of rock beds, Hasnain [10] mentioned that an approximate rule is to use 300–500 kg (resp. 130–250 m^3) of rock per square meter of solar collector area. King and Burns [32] studied a number of characteristics such as particle size, void fraction, bed cross-sectional area and bed length, superficial air velocity, and Reynolds number, in order to describe the thermal properties and geometric configurations of packed beds. Choudhury et al. [33] studied the optimization of design and operational parameters of a rock bed thermal energy storage device coupled to a two-pass single-cover solar air heater. The authors investigated parameters such as the charging time, the rock's size, the cross-sectional area, the void fraction, and the air mass velocity per bed cross-sectional area. They concluded that the void fraction and the air mass velocity per bed cross-sectional area are critical and should be chosen depending on the system's operating temperature.

3. Latent heat storage

By definition, latent heat storage is based on the heat absorbed or released when a material undergoes a phase change from one physical state to another. Practically speaking, the phase change can occur in the following forms: solid–solid, solid–liquid, solid–gas, liquid–gas and vice-versa.

During the solid–solid transitions, heat is stored as the material is transformed from one crystalline form to another [34]. Since there is only a change in the crystalline structure, small latent heat and small volume changes are generally observed in comparison to solid–liquid transitions. In return, solid–solid phase change materials (PCMs) present the advantages of having less stringent container requirements and greater design flexibility [35]. During the past decades, relatively few solid–solid PCMs with suitable heats of fusion and transition temperatures for building applications have been identified. One of the most promising is pentaglycerine (melting temperature 81 °C, latent heat of fusion 263 MJ/m^3) [2].

Solid–gas and liquid–gas transitions present higher latent heat values, but the large volume change during the transition leads to more stringent containment requirements; they are not suitable for building heat storage applications [10].

Solid–liquid PCMs have benefited from many developments during the past two decades, although the amount of heat involved during their phase change is smaller than that of solid–gas or liquid–gas PCMs. Solid–liquid PCMs can store and release a relatively large quantity of heat within a narrow temperature range, without a large volume change. Solid–liquid transitions have also proved to be economically attractive [10].

For residential applications, the main purpose of the use of latent heat storage systems is to decrease the temperature fluctuation, particularly the fluctuation due to incident solar radiation loads, as proved in several numerical studies [36–38].

One application of this principle can be found by inserting suitable latent heat storage material into the building thermal mass/ structure. In this context, intensive research work pertaining to the effective use of PCM impregnated-wallboards in interior wall surfaces of the building enclosure has been conducted in recent years [11,34,38–45]. Table 2 presents a review of some research work on the integration of PCMs within buildings elements and systems.

Table 2
Summary of research work on integrated latent heat energy storage systems in buildings.

Application	PCM Type	Material	Latent heat storage system	Description	Methodology	References
HEATING	Inorganic	$CaCl_2 \cdot 6H_2O$	Floor component	Under-floor heating system with encapsulated PCM placed in the concrete floor during construction	Experiment	[193]
	Inorganic Organic	$CaCl_2 \cdot 6H_2O$ $LiNO_3 \cdot 3H_2O$ paraffin wax RT25	Facade panel	PCM blended with glazing panels to improve day lighting, space heating and thermal comfort in winter; reduces peak cooling loads in summer	Experimental	[194]
	Organic	High density polyethylene Polyethylene wax	Floor component	Cost-effective novel form stable PCM containing microencapsulated paraffin regulates indoor temperature	Simulation	[195]
	Organic	Paraffin RT-20	Internal wall and ceiling construction	PCM implanted gypsum boards to store heat energy from existing electrical facility in office space; shift on-peak space heating demand and conserve overall electrical energy	Experiment	[196]
	Organic	Shape-stabilized paraffin	Floor component	Cost-effective shape stabilized PCM plates stores heat in night time using off-peak electricity to compensate on-peak space heating demand in daytime	Experiment	[197]
	–	–	Internal wall construction	Diurnal/short-term heat storage from direct heat gain in a residential building room	Simulation	[198]
	Organic	Mixture of Capric acid (82%) and lauric acid (18%)	Internal wall construction	Wallboards consisting of combining gypsum boards with phase change materials (PCM) are formed. Then, the thermal properties of phase change wallboards are analyzed. The phase change wall room and the ordinary wall room are experimented and compared under the same climatic conditions.	Experiment	[14]
COOLING	Inorganic Organic	SP-25 A8 Paraffin RT 27	Brick construction	Encapsulated PCM offsets cooling demand from building; to conserve overall electrical energy consumption and reduce CO_2 emission from building	Experiment	[199]
	Organic	Paraffin RT 25	Ceiling mounted	PCM stores cool energy from ambient air during night time for meeting out daytime cooling demand	Experiment	[200]
	Inorganic	$Mn(NO_3)_2 \cdot 6H_2O$	Stainless steel vessel	PCM thermal energy response during regeneration from cold energy source such as cool outside air cooling during night.	Experiment	[201]
	Organic	Paraffin	Exterior wall	PCM-doped color coatings applied on building exterior fabric minimizes indoor temperature variations, reduces building thermal load; to maintain thermal comfort conditions in indoor space	Experiment	[202]
	Organic	Fatty acid	Ceiling mounted	Night ventilation scheme amalgamated with PCM packed bed storage reduces room temperature in day hours and conserve energy spent on cooling and ventilation	Experiment	[203]
	Organic	Paraffin waxes	Floor component	PCM granules made of glass beads and paraffin waxes stores large cooling energy in night time to release it upon demand during day-peak load periods	Experiment	[204]
	Organic	Paraffin RT20	Ceiling mounted	Two separate LHES systems containing sphere encapsulated PCM stores cool energy to reduce heat gain from ventilation air and room return air; save overall building energy, regulate indoor temperature and reduce size of mechanical ventilation system	Experiment	[205]
	Organic	n-octadecane n-eicosane P116	Brick construction	Brick element with cylindrical holes filled with PCM to absorb direct heat gain and reduces temperature fluctuations in indoor environment	Simulation and experiment	[206]
	Inorganic Organic	–	Ceiling mounted	PCM integrated with air heat exchanger to cool indoor air during day-peak load conditions with stored cool energy in night time	Experiment	[207]
	Organic	Heptadecane	Ceiling panel	Ceiling panels embedded with PCM to cool indoor environment	Experiment and simulation	[208]

Table 3
Comparison of various heat storage media (for sensible storage materials, energy is stored in the temperature range 25–75 °C, adapted from Hasnain et al. [10]).

Property	**Heat storage material**			
	Sensible heat storage		Phase change materials	
	Rock	Water	Paraffin wax	$CaCl_2 \cdot 6H_2O$
Latent heat of fusion (kJ/kg)	*	*	174.4	266
Specific heat capacity (kJ/(kg K))	0.9	4.18	–	–
Density (kg/m^3) at 24 °C	2240	1000	1802	795
Storage volume for storing 1 GJ (m^3)	9.9	4.8	3.2	4.7
Relative volume**	3.1	1.5	1.0	1.5

(–) Specific heat capacity is not of interest for latent heat storage.

* Latent heat of fusion is not of interest for sensible heat storage.

** Equivalent storage volume, reference taken on paraffin.

Globally, latent heat storage systems have a number of advantages over sensible heat storage systems: a volumetric heat storage density, which is high, and the operating temperature, which is relatively constant for PCM systems but can vary widely for sensible systems corresponding to the load. As shown in Table 3, for the same amount of heat stored, latent heat storage systems using paraffin wax will need 1.5 times (resp. 3 times) less volume than sensible heat storage systems using water (resp. rocks)

Table 4
Commercial PCMs suitable for residential applications.

Application	PCM type	Designation	Melting temperature (°C)	Heat of fusion (kJ/kg)	C_p (kJ/(kg K))	k (W/(m K))	ρ** (kg/m^3)	Manufacturer*	References
COOLING	**INORGANICS**	S10	10	155	1.90	0.430	1470	A	[209]
		ClimSel C10	10.5	126	3.60	0.5–0.7	1420	B	[210]
		S13	13	160	1.90	0.430	1515	A	[209]
		S15	15	160	1.90	0.430	1510	A	[209]
		S17	17	160	1.90	0.430	1525	A	[209]
		S19	19	160	1.90	0.430	1520	A	[209]
		S21	22	170	2.20	0.540	1530	A	[209]
		ClimSel C21	21	144	3.60	0.5–0.7	1380	B	[210]
		S23	23	175	2.20	0.540	1530	A	[209]
		ClimSel C24	24	126	3.60	0.5–0.7	1380	B	[210]
		S25	25	180	2.20	0.540	1530	A	[209]
		S27	27	183	2.20	0.540	1530	A	[209]
		ClimSel C28	28	162	3.60	0.5–0.7	1420	B	[210]
		S30	30	190	1.90	0.480	1304	A	[209]
	ORGANICS	A15	15	130	2.26	0.180	790	A	[209]
		A17	17	150	2.22	0.180	785	A	[209]
		RT21	21	134	–	0.2	880 (s, 15 °C) 770 (liq, 25 °C)	C	[211]
		A22	22	145	2.22	0.180	785	A	[209]
		A23	23	145	2.22	0.180	785	A	[209]
		A24	24	124	2.22	0.180	790	A	[209]
		A25	25	150	2.26	0.180	785	A	[209]
		A26	26	150	2.22	0.210	790	A	[209]
		RT27	27	184	–	0.2	880 (s, 15 °C) 760 (liq, 40 °C)	C	[211]
		A28	28	155	2.22	0.210	789	A	[209]
		RT28	28	245	–	0.2	880 (s, 15 °C) 768 (liq, 40 °C)	C	[211]
	EUTECTICS	SP 22 A17	22–24	150	–	0.6	1490 (s, 20 °C) 1420 (liq, 40 °C)	C	[211]
		SP 25 A8	25–27	160	–	0.6	1430 (s, 20 °C) 1230 (liq, 40 °C)	C	[211]
		SP 26 A9	26–28	170	–	0.6	1460 (s, 20 °C) 1440 (liq, 40 °C)	C	[211]
		SP 29 A15	28–30	190	–	0.6	1530 (s, 25 °C) 1510 (liq, 45 °C)	C	[211]
HEATING	**INORGANICS**	S32	32	200	1.91	0.510	1460	A	[209]
		ClimSel 32	32	162	3.6	0.5–0.7	1420	B	[210]
		S34	34	115	2.10	0.520	2100	A	[209]
		S44	44	100	1.61	0.430	1584	A	[209]
		S46	46	210	2.41	0.450	1587	A	[209]
		ClimSel 48	48	216	3.6	0.5–0.7	1360	B	[210]
		S50	50	100	1.59	0.430	1601	A	[209]
		S58	58	145	2.55	0.690	1505	A	[209]
		ClimSel 58	58	288	3.6	0.5–0.7	1360	B	[210]
		S72	72	127	2.13	0.580	1666	A	[209]
		S83	83	141	2.31	0.620	1600	A	[209]
		ClimSel 70	70	396	3.6	0.6–0.7	1700	B	[210]
	ORGANICS	A32	32	130	2.20	0.210	845	A	[209]
		A39	39	105	2.22	0.220	900	A	[209]
		A42	42	105	2.22	0.210	905	A	[209]
		P116	46.7–50	209	2.89	0.277 (liq) 0.140 (s)	786 (s)	–	[82,212,213]
		A53	53	130	2.22	0.220	910	A	[209]
		A55	55	135	2.22	0.220	905	A	[209]
		A58	58	132	2.22	0.220	910	A	[209]
		A60	60	145	2.22	0.220	910	A	[209]
		A62	62	145	2.2	0.220	910	A	[209]
		A70	70	173	2.2	0.230	890	A	[209]
		A82	82	155	2.21	0.220	850	A	[209]
		A95	95	205	2.2	0.220	900	A	[209]

(–): not available.

* A=EnvironmentalProcess Limited; B=Climator AB; C=Rubitherm;

** s=solid, liq=liquid.

as heat storage material with a 50 °C temperature change. The performances of latent heat storage systems are strongly dependent on the thermophysical properties of the PCMs employed. However, there are a number of disadvantages associated with latent heat storage materials. Low thermal conductivity, material stability over several cycles, phase segregation, subcooling, and finally cost are some of these limitations that are currently under investigation [18,34,43,46–62]. In Jegadheeswaran and Pohekar [62], a detailed review of enhancement techniques of latent heat storage and their influence on the thermal response of PCMs in terms of amount and rate of latent heat stored/retrieved has been reported. The authors reviewed various techniques such as extended surfaces, employing multiple PCMs, thermal conductivity enhancement, and micro-encapsulation and assessed their effect on the thermal response of latent heat storage units. Table 4 shows a classification of commercial commonly used PCMs with respect to their thermophysical properties and respective manufacturers [63]. PCMs suitable for space cooling have their melting point ranging from 10 to 30 °C, and those suitable for space heating a melting point ranging from 30 to 100 °C.

3.1. Phase change materials, classification and properties

Table 5 presents a glimpse of the main criteria which should govern the selection of solid–liquid PCMs. The most important of them are the melting temperature (which should be in the operating range), substantial latent heat and high thermal conductivity in order to store or release heat. However, the majority of PCMs does not satisfy either of the last two conditions.

PCMs can be classified into the following major categories: inorganic PCMs, organic PCMs, and eutectic PCMs. Each of these groups can be further categorized into more detailed subgroups as shown in Fig. 3. The inorganic group of PCMs is composed of salt hydrates and metals, whereas the organic group is composed of paraffins and non-paraffins. Eutectics are mixtures of inorganics and/or organics. Each of these groups has its typical range of melting temperature and melting enthalpy.

3.2. Inorganic phase change materials

Inorganic PCMs are constituted of salt hydrates and metals. Salt hydrates have been the most thoroughly investigated for heat storage purposes in dwellings.

3.2.1. Salt hydrates

Salt hydrates can be considered as alloys of inorganic salts (AB) and water (H_2O), resulting in a typical crystalline solid with a general formula ($AB \cdot xH_2O$) [34]. Their phase change transition can actually be regarded as a dehydration or hydration of the salt, although this process is similar to melting or freezing the compound. Salt hydrates usually melt to either a salt hydrate with fewer moles of water or its anhydrous form [34]. During the phase change transition, liquid water released from the hydrated salt dissolves the formed non-hydrated salt molecules. As shown in Table 6, salt hydrates are attractive for heat storage purposes in dwellings because they have a high volumetric storage density ($\sim$350 MJ/m^3) and a relatively high thermal conductivity (0.5 W/(m K)) compared to organic PCMs (as shown in Table 8). Also, salt hydrates are cheaper.

However, a major problem with salt hydrates may result from the decrease of their energy storage density with cycling. Incongruent melting is one of the causes of this problem. Sharma [34] describes it as follows: during the melting of most salt hydrates, the released water is not sufficient to dissolve all the crystals present. Consequently, due to their density, crystals settle at the bottom of the container and will not reform a hydrated crystal during the subsequent solidification of the compound. This causes irreversibility in the process. A solution to this problem is found in the literature in the application of one of the following methods:

- The use of excess water, which would prevent the clogging of the solution and the formation of an anhydrous salt, but this will decrease the storage density of the system [64];
- The addition of thickening agents (such as Bentonite, Borax [65,66]) which prevents the deposit of crystals by holding them in suspension; unfortunately this solution will result in a lower thermal conductivity of the mixture with consequently reduced rates of heat transfer and crystallization;
- The encapsulation of the PCM to reduce phase separation [62,67];
- The mechanical stirring of the mixture [68].

Subcooling before crystallization is another serious problem associated with hydrated salts. Several techniques such as the use of nucleating agents [69], the promotion of nucleation by rough container walls or by using the cold finger technique [49,66,70],

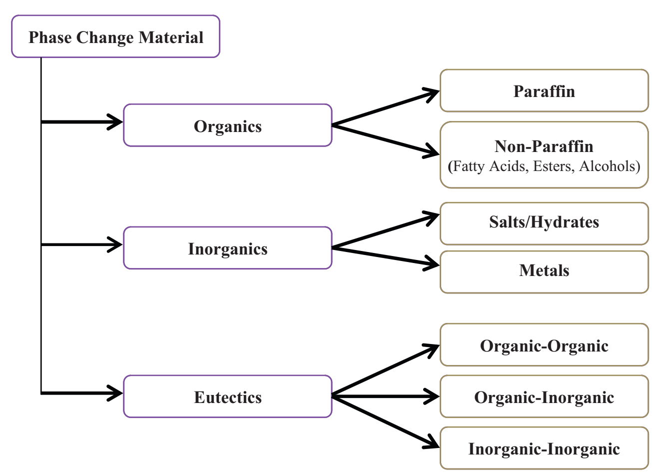


Fig. 3. Classification of phase change materials.

Table 5
Most important features required for PCMs [83].

Properties	PCMs		
Thermal	Phase change temperature fitted to application	High phase change enthalpy near temperature of use	High thermal conductivity in both liquid and solid phases (although not always)
Physical	Low density variation	High density	Small or no sub-cooling
Chemical	Stability	No phase separation	Compatibility with container materials, Nontoxic,…. non-flammable, non-polluting
Economic	Cheap and abundant		

Table 6
Inorganic substances with potential use as PCM for residential applications.

Application	Compound	Type of melting*	Melting temperature °C	Heat of fusion kJ/kg	C_p ** (kJ/(kg K))	k ** (W/(m K))	ρ ** kg/m^3	Reference
COOLING	$LiClO_3 \cdot 3H_2O$	c	8.1	253	1.35 (s)	–	1720	[214,215]
	$ZnCl_2 \cdot 3H_2O$	–	10	–	–	–	–	[216]
	$K_2HPO_4 \cdot 6H_2O$	–	13	–	–	–	–	[217]
	$NaOH \cdot 7/2CO_2$	–	15	–	–	–	–	[217]
	$Na_2CrO_4 \cdot 10H_2O$	–	18	–	1.31 (s)	–	–	[215,217]
	$KF \cdot 4H_2O$	c	18.5	231	1.84 (s)	–	1447 (liq, 20 °C) 1455 (s, 18 °C)	[39,44,46,47,214]
	$Mn(NO_3)_2 \cdot 6H_2O$	–	25.8	125.9	–	2.34 (s)	1800 (liq,20 °C)	[201]
	$CaCl_2 \cdot 6H_2O$	i	29	188.34	1.43 (s) 2.31 (liq)	0.540 (liq, 38.7 °C) 0.561 (liq, 61.2 °C) 1.09 (s, 23 °C)	1562 (liq,32 °C) 1802 (s, 24 °C)	[18,44,218–220]
HEATING	$LiNO_3 \cdot 3H_2O$	–	30	296	–	0.58 (liq) 1.37 (s)	1780 (liq) 2140 (s)	[83,214]
	$Na_2CO_3 \cdot 10H_2O$	i	32–36 33	246.5 247	1.79 (s)	–	1442	[65,214–216]
	$Na_2SO_4 \cdot 10H_2O$	i	32.4	251	1.44 (s)	0.5–0.7	1420	[215,216]
	$CaBr_2 \cdot 6H_2O$	i	34	115.5	–	–	1956 (liq, 35 °C) 2194 (s,24 °C)	[18,216,219]
	$K(CH_3COO) \cdot 3/2H_2O$	–	42	–	–	–	–	[217]
	$K_3PO_4 \cdot 7H_2O$	–	45	–	–	–	–	[217]
	$Zn(NO_3)_2 \cdot 6H_2O$	c	36.4	147	1.34 (s) 2.26 (liq)	–	2065 (14 °C)	[46,217]
	$Ca(NO_3)_2 \cdot 4H_2O$	i	42.7	–	–	–	–	[221]
	$Na_2HPO_4 \cdot 7H_2O$	i	48	281	1.70 (s) 1.95 (liq)	0.514 (32 °C) 0.476 (49 °C)	1520 (s) 1442 (liq)	[46,221]
	$Na_2S_2O_3 \cdot 5H_2O$	i	48–49 48	209.3 201–206	3.83 (liq)	–	1666	[218,222]
	$Zn(NO_3)_2 \cdot 2H_2O$	c	54	–	–	–	–	[217]
	$NaOH \cdot H_2O$	c	58.0	–	2.18 (s)	–	–	[215,221]
	$Na(CH_3COO) \cdot 3H_2O$		58	226 267	– 2.79–4.57	– 0.63 (s)	1450 1280	[223,214,224]
	$Cd(NO_3)_2 \cdot 4H_2O$	c	59.5	–	–	–	–	[221]
	$Fe(NO_3)_2 \cdot 6H_2O$	-	60	–	–	–	–	[217]
	$Na_2B_4O_7 \cdot 10H_2O$	i	68.1	–	–	–	–	[221]
	$Na_3PO_4 \cdot 12H_2O$	i	69	–	–	–	–	[221]
	$Ba(OH)_2 \cdot 8H_2O$	i	78	265.7		0.653 (liq, 85.7 °C), 0.678 (liq, 98.2 °C)	1937 (liq, 84 °C) 2070 (s, 24 °C)	[18,46,214,216,219,223]
	$KAl(SO_4)_2 \cdot 12H_2O$	i	80	–	–	–	–	[217]
	$Al_2(SO_4)3 \cdot 18H_2O$	–	85.8	–	–	–	–	[216]
	$Al(NO_3)_3 \cdot 8H_2O$	–	88	–	–	–	–	[217]

(–): not available.

* c = congruent, i = incongruent;

** s = solid, liq = liquid.

the use of rotating storage devices, and a direct contact heat transfer have been used to prevent this problem [47,71–75].

3.2.2. Metals

Table 7 shows the thermal features of selected metals with a low melting temperature as members of the group of inorganic PCMs. Most of them are fusible alloys of bismuth with other metals such as lead, tin, indium, and cadmium. As a general rule, the physical properties of these alloys will be close to those of bismuth with some differences related to the addition of the other compounds. The use of metals as energy storage media has several drawbacks, such as their scarce availability and their high cost. However, when volume is a constraint, they are good candidates because of their high volumetric fusion heat [34]. Another advantage of these materials on other PCMs is their high thermal conductivity.

3.3. Organic phase change materials

Organic heat storage materials are usually separated into two groups: paraffins, which are mixtures of alkanes, and non-paraffin organic materials, which include fatty acids, some alcohols, and esters.

3.3.1. Paraffins

Paraffins can be defined as a mixture of pure alkanes, mostly straight-chain configured. The crystallization/fusion of their molecular chain involves a large amount of latent heat. They are usually referred to as "paraffin waxes" with the chemical formula C_nH_{2n+2}, where $20 \leq n \leq 40$. The melting temperature of these compounds increases with the number of alkane chains present within the molecule. Studies conducted over recent years on PCMs have produced the results presented in Table 8. The average heat of paraffin fusion suitable for building applications is 170 MJ/m^3 and is almost half the value of that of hydrated salts. However, paraffins present negligible supercooling, non-corrosiveness, chemical stability, self-nucleation, no phase segregation, and low cost operation [10,46,49,76]. Their low thermal conductivity (~0.2 W/(m K)) and the significant volume change occurring during their phase change are their major drawbacks. To overcome these disadvantages, several techniques such as metallic fillers, metal matrix structures, finned tubes, aluminum shavings, and encapsulated containers have been reported in the literature [50,76–79]. Marin et al. [80], and Mettawee and al. [81] investigated experimentally the enhancement of the thermal conductivity of paraffin wax by embedding aluminum powder in it. The experiments were conducted by using a compact PCM

Table 7
Melting point and latent heat of fusion of some metal alloys used in residential heat storage applications.

Material	Composition (%)	Melting temp. (°C)	Heat of fusion (kJ/kg)	C_p* k(J/(kg K))	k^{a*} W/(m K)	ρ (kg/m^3)	References
Gallium	–	30.0	80.3	0.83 (s/liq)	40.6 (s)	5910	[225]
Cerrolow 117	Bismuth 44.7 Lead 22.6 Tin 8.3 Cadmium 5.3 Indium 19.1	47.2	68.175	0.15 (s/liq)	16.7 (s)	8860	[226]
Cerrolow 136	Bismuth 49 Lead 16 Tin 12 Indium 21	58	90.9	0.13 (s/liq)	16.7 (s)	8570	[226]
Cerrolow 158	Bismuth 50 Lead 26.7 Tin 13.3 Indium 10	70	159	0.17 (s/liq)	16.7 (s)	9380	[226]
Cerrolow 203	Bismuth 52.5 Lead 32 Tin 15.5	95	–	–	–	9850	[226]

(–): not available;
a = approximate.
* s = solid, liq = liquid.

solar collector where an absorber-container unit was dedicated to absorb the solar energy and store it in the phase change material (PCM). The discharge was realized by cold water flowing in pipes located inside the PCM. The rate of temperature change was recorded during the charging and discharging. As a result, the authors found that there is an increase of the useful heat gained when adding aluminum powder in the wax as compared to the pure paraffin wax. Benmansour and al. [79] investigated experimentally and mathematically both charging and discharging processes using paraffin wax as a storage medium encapsulated in spheres inside a cylindrical tank. Their numerical model has predicted precisely the temperature distribution within the bed during both charging and discharging. Using a mathematical model, Arkar and Medved [78] studied the influence of accuracy of thermal property data of a phase change material on the result of a numerical model of a packed bed heat storage system. Numerical results were verified experimentally with a cylindrical heat storage reactor of 0.34 m of diameter, 35 rows of hollow polyethylene spheres filled with RT20 paraffin from Rubitherm GmbH. The height of the system was 1.52 m and the packed bed's average porosity was 0.388. Charge and discharge of the system were realized at different flow rates: 166 and 76 m^3/h during the discharge processes and 108 and 215 m^3/h during the charge processes. From the comparison of numerical with experimental results, the author found that the mathematical expression of the apparent heat capacity, a parameter that describes how the latent heat of the PCM evolves over the temperature range, should include a heating or cooling rate as an additional parameter. The rate of temperature change of the PCM was analyzed, and as a result they found that on average it does not exceed 0.1 K/min both during charging (inlet flow at 33 °C on average) and discharging (inlet flow at 11 °C on average).

Pure paraffins are very expensive and therefore only technical grade paraffins (mixture of pure substances) are used for latent heat storage applications [34]. P-116 (Table 4), a mixture of C_{20} through C_{32} hydrocarbons, is a commercial paraffin wax that has been used by a wide number of investigators [82–85]. It has a melting temperature of 47 °C and a latent heat of fusion of 202 MJ/m^3. In general, technical grade paraffins have a melting/freezing temperature range rather than a sharp melting/freezing point, but the characteristics available from manufacturers seldom provide this precise information.

3.3.2. Non-paraffin organic PCMs

Non-paraffin organic PCMs are made up of compounds such as fatty acids, esters, and alcohols [10,34]. They are highly flammable and therefore should not be exposed to intense temperature, flames, and oxidizing agents [34]. This is their main drawback for a use as heat storage materials in buildings. Other features of these organic materials are reproducible melting and freezing behavior, freezing with no super-cooling, low thermal conductivity, and a varying level of toxicity [34,60].

Among non-paraffin organic PCMs, fatty acids have interested specialists the most. One of the reasons is that they are relatively cheap, although their cost still remains 2–2.5 times greater than that of technical grade paraffins. Numerous authors such as Abhat et al.[86], Buddhi and Sawhney[87], Feldman et al. [88–91] and Hasan [92] have conducted experiments on a number of fatty acids. Table 8 lists data from these investigations. The melting points of fatty acids vary from 10 to 70 °C [93]. Their volumetric heat of fusion which ranges from 128 to 183 MJ/m^3, is comparable to that of paraffins.

3.4. Eutectics

Eutectics are alloys of inorganics (mostly hydrated salts) and/or organics. They have a single melting temperature, which is usually lower than that of any of the constitutive compounds. Eutectics form a single common crystal when crystallized [10,34]. One of the most important characteristics of eutectics is their capability to melt/freeze congruently without phase segregation. A large number of eutectics have been reported throughout the literature and classified as inorganic eutectics, organic eutectics, and organic–inorganic eutectics [49,94]. Shilei et al. [95] report a comparative study between an ordinary room and a PCM integrated-wall room. A mixture of capric acid and lauric acid (with respective melting and freezing temperature of 19.14 and 20.40 °C) in the proportion of 82/18% is used. The room integrated with this PCM impregnated wallboards shows good performance in terms of thermal comfort during winter. Also, the heat losses from the room to the ambient area in winter are significantly reduced.

A list of eutectics suitable for building applications is presented in Table 9. Organic eutectics generally have a lower melting temperature and a greater fusion heat than inorganic eutectics, making them adequate for heat storage needs in building applications.

Table 8
Organic substances with potential use as PCM for residential applications.

Group		Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	C_p (kJ/(kg K))	k* (W/(m K))	ρ* (kg/m^3)	References
PARAFFIN	**COOLING**	Paraffin C14	4.5	165	–	–	–	[46]
		Paraffin C15–C16	8	153	2.2 (s)	–	–	[46,227]
		Polyglycol E400	8	99.6	–	0.187 (liq,38.6 °C) 0.185 (liq, 69.9 °C)	1125 (liq, 25 °C) 1228 (s, 3 °C)	[18,219]
		Dimethyl-sulfoxide (DMS)	16.5	85.7	–	–	1009 (s/liq)	[228]
		Paraffin C17–C18	20–22	152	2.2 (s)	–	–	[227,229]
		Polyglycol E600	22	127.2	–	0.189 (liq, 38.6 °C) 0.187 (liq, 67.0 °C)	1126 (liq, 25 °C) 1232 (s, 4 °C)	[18,219]
		Paraffin C13–C24	22–24	189	2.1 (s)	0.21 (s)	760 (liq, 70 °C) 900 (s, 20 °C)	[44,46]
		1-dodecanol	26	200	–	–	–	[39]
		Paraffin C18	28 27.5	244 243.5	2.2 (s)	0.148 (liq, 40 °C) 0.15 (s)	774 (liq, 70 °C) 814 (s, 20 °C)	[46,227,230]
	HEATING	Paraffin C20–C33	48–50	189	–	0.21 (s)	769 (liq, 70 °C) 912 (s, 20 °C)	[46]
		Paraffin C22–C45	58–60	189	2.4 (s)	0.21 (s)	795 (liq, 70 °C) 920 (s, 20 °C)	[46,231]
		Paraffin wax	64	173.6 266	–	0.167 (liq, 63.5 °C) 0.346 (s, 33.6 °C) 0.339 (s, 45.7 °C)	790 (liq, 65 °C) 916 (s, 24 °C)	[18,219,214]
		Polyglycol E6000	66	190.0	–	–	1085 (liq, 70 °C) 1212 (s, 25 °C)	[18,219]
		Paraffin C21–C50	66–68	189	–	0.21 (s)	830 (liq, 70 °C) 930 (s, 20 °C)	[46]
		1-Tetradecanol	38	205	–	–	–	[39]
		Paraffin C16–C28	48–50	189	–	0.21 (s)	765 (liq, 70 °C) 910 (s, 20 °C)	[46]
		Biphenyl	71	119.2	–	–	991 (liq, 73 °C) 1166 (s, 24 °C)	[18,219]
		Propionamide	79	168.2	–	–	–	[219]
		Naphthalene	80	147.7	2.8 (s)	0.132 (liq, 83.8 °C) 0.341 (s, 49.9 °C) 0.310 (s, 66.6 °C)	976 (liq, 84 °C) 1145 (s, 20 °C)	[18,219,232]
FATTY ACIDS	**COOLING**	Propyl palmiate	10 16–19	186	–	–	–	[39,42]
		Caprylic acid	16 16.3	148.5 149	–	0.149 (liq, 38.6 °C) 0.145 (liq, 67.7 °C) 0.148 (liq, 20 °C)	901 (liq, 30 °C) 862 (liq, 80 °C) 981 (s, 13 °C) 1033 (s, 10 °C)	[18,219,46]
		Isopropyl palmiate	11	95–100	–	–	–	[233]
		Capric–lauric acid +pentadecane (90%–10%)	13.3	142.2	–	–	–	[234]
		Isopropyl stearate	14–18	140–142	–	–	–	[233]
		Capric–lauric acid (65%–35%)	18.0 17–21	148 143	–	–	–	[235,42]
		Butyl stearate	19	140	–	–	–	[39]
		Capric–lauric acid (45%–55%)	21	143	–	–	–	[39]
		Dimethyl sabacate	21	120–135	–	–	–	[233]
		Octadecyl 3-mencaptopropylate	21	143	–	–	–	[41]
		Mystiric acid-Capric acid (34%–66%)	24	147.7	–	0.164 (liq, 39.1 °C) 0.154 (liq, 61.2 °C)	888 (liq, 25 °C) 1018 (s)	[219]
		Octadecylthioglycate	26	90	–	–	–	[41]
	HEATING	Vinyl stearate	27–29	122	–	–	–	[233]
		Lauric acid	42–44 44	178 177.4	2.3 (liq) 1.7 (s)	0.147 (liq, 50 °C)	862 (liq, 60 °C) 870 (liq, 50 °C)	[46,219]
		Myristic acid	49–51 54 58	204.5 187 186.6	2.4(liq) 1.7(s)	–	861 (liq, 55 °C) 844 (liq, 80 °C) 990 (s, 24 °C)	[236,46,237,219]
		Palmitic acid	64 61 63	185.4 203.4 187	2.8(liq) 1.9(s)	0.162 (liq, 68.4 °C) 0.159 (liq, 80.1 °C) 0.165 (liq, 80 °C)	850 (liq, 65 °C) 847 (liq, 80 °C) 989 (s, 24 °C)	[18,219,237,238,239,46]
		Stearic acid	69 60–61 70	202.5 186.5 203	2.2 (liq) 1.6 (s)	0.172 (liq, 70 °C)	848 (liq, 70 °C) 965 (s, 24 °C)	[18,219,237,239,46]

(–)=not available.

* s=solid, liq=liquid.

3.5. Composite PCMs

Composite PCMs can be defined as form stable mixtures of PCMs with others materials which act as supporting materials. Sari et al.[96] performed the preparation, characterization, and determination of thermal energy storage properties of poly (n-butyl methacrylate) (PnBMA)/fatty acid composites as form-stable PCM. In the composite, the PnBMA acts as the host material

Table 9
Thermal properties of some eutectics PCMs suitable for residential applications.

Group	Application	Compound	Composition	Melting temperature (°C)	Heat of fusion (kJ/kg)	k* W/(m K)	ρ* kg/m^3	References
INORGANICS	**COOLING**	$CaCl_2 \cdot 6H_2O + CaBr_2 \cdot 6H_2O$	45+55	14.7	140	–	–	[34]
		$CaCl_2 + MgCl_2 \cdot 6H_2O$	66.3+33.3	25	95	–	1590	[214]
	HEATING	$Ca(NO_3) \cdot 4H_2O + Mg(NO_3)_3 \cdot 6H_2O$	47+53	30	136	–	–	[34]
		$Mg(NO_3)_3 \cdot 6H_2O + NH_4NO_3$	61.5+38.5	52	125.5	0.494 (liq,65.0 °C) 0.515 (liq,88.0 °C)	1515 (liq,65 °C) 1596 (s,20°C)	[219]
		$Mg(NO_3)_3 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$	58.7+41.3	59	132.2	0.510 (liq, 65.0 °C) 0.565 (liq, 88.0 °C)	1550 (liq, 50 °C) 1630 (s, 24 °C)	[34]
		$Mg(NO_3)_3 \cdot 6H_2O + MgCl_2 \cdot 6H_2O$	50+50	59.1	144	–	–	[34]
		$Mg(NO_3)_3 \cdot 6H_2O + Al(NO_3)_2 \cdot 9H_2O$	53+47	61	148	–	1850	[41]
		$Mg(NO_3)_2 \cdot 6H_2O + MgBr_2 \cdot 6H_2O$	59+41	66	168	–	–	[34]
		$LiNO_3 + NH_4NO_3 + NaNO_3$	25+65+10	80.5	113	–	–	[34]
		$LiNO_3 + NH_4NO_3 + KNO_3$	26.4+58.7+14.9	81.5	116	–	–	[34]
		$LiNO_3 + NH_4NO_3 + NH_4Cl$	27+68+5	81.6	108	–	–	[34]
ORGANICS	**COOLING**	Triethylolethane+water+urea	38.5+31.5+30	13.4	160	–	–	[34]
		$C_{14}H_{28}O_2 + C_{10}H_{20}O_2$	34+66	24	147.7	–	–	[34]
	HEATING	$CH_3CONH_2 + NH_2CONH_2$	50+50	27	163	–	–	[34]
		Triethylolethane+urea	62.5+37.5	29.8	218	–	–	[34]
		$CH_3COONa \cdot 3H_2O + NH_2CONH_2$	40+60	30	200.5	–	–	[34]
		$NH_2CONH_2 + NH_4NO_3$	53+47	46	95	–	–	[34]
		$CH_3CONH_2 + C_{17}H_{35}COOH$	50+50	65	218	–	–	[34]
		Naphthalene+benzoic acid	67.1+32.9	67	123.4	–	–	[34]
		$NH_2CONH_2 + NH_4Br$	66.6+33.4	76	151	–	–	[34]

* s=solid, liq=liquid, (–)=not available.

Table 10
Thermal energy storage properties of pure fatty acids and form-stable composite PCMs [96].

Form-stable composite PCM	Melting temperature°C	Heat of melting (kJ/kg)	Freezing temperature (°C)	Heat of freezing (kJ/kg)
CA	31.35	172.40	25.86	172.67
LA	44.15	178.74	41.48	177.66
MA	54.39	196.04	51.45	198.30
PA	62.73	217.45	58.82	213.98
PnBMA/CA	29.62	67.23	27.65	67.09
PnBMA/LA	41.69	71.12	38.47	71.02
PnBMA/MA	45.97	77.27	41.79	78.35
PnBMA/PA	53.73	86.34	50.46	85.32

and also allows preventing the leakage of the fatty acid when melted. Four fatty acids were used during the tests: capric acid (CA, 98% pure, melting temperature: 32.14 °C), lauric acid (LA, 98% pure, melting temperature: 44.15 °C), myristic acid (MA, % pure, melting temperature: 52.44 °C) and palmitic acid (PA, 98% pure, melting temperature: 61.70 °C). The encapsulation ratio of fatty acid inside all the samples was chosen to be 40 wt% because of the leakage problem occurring over this value. The composite was prepared with the solution polymerization method. Melting and solidification tests were performed at a rate of 5 °C/min respectively and constant stream of nitrogen, used as the heat transfer fluid, at a flow rate of 60 mL/min. As presented in Table 10, results of melting (resp. freezing) experiments showed a small decrease (resp. increase) in phase change temperature of the form stable composites compared to that of pure fatty acids. The latent heat values of the composites were also found to be slightly lower. The author found an explanation in the formation of intermolecular hydrogen bond between the –OH group of fatty acid and the carbonyl group of PnBMA.

More studies on composites PCMs such as paraffin/polyethylene [97–99], poly (ethylene glycol) (PEG)/acrylic polymer [100], fatty acid/ poly (n-methyl methacrylate) (PMMA) [101], lauric acid/ poly (ethylene terephthalate) (PET) [102], fatty acid/styrene maleic anhydride (SMA) [103], fatty acid/polyethers [104], stearyl stearate/PET [105], fatty acid/eudragit [106], paraffin/polypropylene [107], fatty acid/PET [108], and PEG/ poly(vinyl chloride) (PVC) [109] have been investigated during recent years.

4. Thermochemical heat storage materials

Throughout the literature one finds several terms or expressions that describe heat storage by chemical or thermochemical processes: "chemical storage," "thermochemical storage," and "sorption" [110–117]. Bales et al.[111] and N'Tsoukpoe et al. [118] attempted to clarify these concepts and the distinction between storage using chemical reactions and sorption phenomena.

Chemical energy storage consists of using a source of energy to excite a reversible chemical reaction [11]. This source can be thermal (thermochemical reactions), electrical (electrochemical reactions such as in batteries), or electromagnetic (photochemical reactions and photosynthesis) [2,119–121]. Chemical reactions are characterized by a change in the molecular configuration of the compound involved during the reactions (dissociation and recombination). The stored energy can be recovered by reversing the reaction, sometimes by adding a catalyst. In thermochemical heat storage, the reaction usually involves a solid and a gas that can react. In building applications, the gas involved is usually water vapor.

Sorption can be defined as a phenomenon of fixation or capture of a gas or a vapor (called sorbate) by a substance in a condensed state (solid or liquid) called sorbent [122,123]. As explained by Srivastava et al. [124], it is a surface phenomenon occurring at the interface of two phases, in which cohesive forces including van der Waals forces and hydrogen bonding act between the molecules of all substances irrespective of their state of aggregation. Unlike chemical reactions, there is no change in the molecular configuration of the compounds. The term "sorption" is a general term that usually refers to both absorption and adsorption

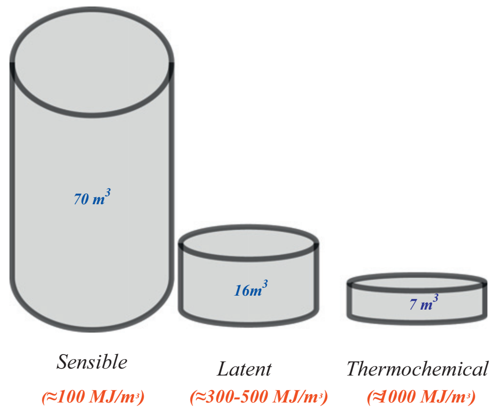


Fig. 4. Volume needed to full cover the annual storage need of an energy efficient passive house (6480 MJ).

[123,125]. In heat storage, absorption (resp. adsorption) designates a sorption phenomenon where the sorbent is a liquid (resp. a solid). In the literature, most of the sorption processes that have been studied involved metal salts with water, ammonia, methanol, or methyl-ammonia as well as metal alloys with hydrogen [126]. In Cot-Gores et al.[126], a classification of the sorbents tested in prototypes under practical conditions for the last two last decades can be found. For building applications, water is also usually used as the sorbate substance. It meets the requirements of a safe system with no risks for the environment. Therefore, hydrophilic substances such as silica gel, zeolites, LiBr, LiCl, KBr, $CaCl_2$, $MgCl_2$, etc. are suitable sorbents for sorption applications. During desorption, energy is stored through the breaking of the water–sorbent bond. If needed, water can then be condensed and stored for future use. Heat recovery consists of re-bonding water vapor with the sorbent; this phenomenon is called ad/absorption.

In the following, the materials used both for chemical reactions and sorption phenomena will be called thermochemical materials. The vapor involved will be generally referred to as the sorbate and the solid or liquid as the sorbent.

Fig. 4 shows the comparison of heat storage systems based on sorption or chemical phenomena and the other heat storage methods (sensible and latent). Thermochemical materials have the advantage of high heat storage density, a significant temperature increase, and the possibility of storing the reactants (sorbent and sorbate) at ambient temperature and with no self-discharge. This is a significant advantage for seasonal storage applications.

Desirable properties for good thermochemical materials have been highlighted throughout the literature [127–131]:

- High affinity of the sorbent for the sorbate: this impacts the rate of the reaction;
- Better volatility of the sorbate than the sorbent in absorption;
- High thermal conductivity and high heat transfer with the heat transfer fluid in the case of adsorption;
- Desorption temperature as low as possible;
- Environmental safety, non-toxicity, low global warming potential and ozone depletion potential;
- Non-corrosiveness of materials;
- Good thermal and molecular stability under assigned operating conditions (temperature, pressure);
- Moderate operating pressure range: no excessive pressure conditions and especially no high vacuum.

Despite their high theoretical storage potential (see Fig. 4), thermochemical heat storage systems generally have very low performance when experimented. The main reasons are the poor heat and mass transfers involved and the thermodynamic operating cycle of the processes. In [126], the authors explain that poor heat and mass transfer performance in the system's reactive bed mainly results from the low thermal conductivity of the reactant sorbents (e.g., 0.1–0.5 W/(m K) for metal chlorides [132–134] and about 1 W/(m K) for metal hydrides [135]), with insufficient heat transfer between the reactants and the heat exchanger's wall [117,136] and the swelling and agglomeration phenomena occurring during the sorption process with water [137–139]. To overcome these limitations and therefore enhance the reactor's bed performance, several authors suggest improved processes such as mixing an additive with the sorbent in absorption [140], and the use of porous elaborated materials [136] or natural expanded graphite for chemical reactions [133,141].

The literature reports different scales for the characterization of thermochemical heat storage materials. Actually, the heat storage capacity data of a material depends on its characterization scale (material-scale, reactor-scale, system-scale). In the material-scale characterization, a usually small amount of material (<10 mg) is investigated and the energy density of the material is often given as the ratio of the heat storage capacity to the volume (or mass) of the active substance when fully reacted. "Fully reacted" here means when there is no more heat stored or released by the material during the test, not when the theoretical maximum heat storage capacity is reached. The reactor-scale characterization deals with larger amounts of material (>10 mg) and the heat storage capacity here is expressed as the ratio of the heat stored to the volume of the vessel where the material is introduced. This can take into account the porosity of the sorbent bed, for example. With the system-scale characterization, heat storage capacity is given as the ratio of the heat stored to the volume of all storage vessels required in the global system, including pipes and any separate vessels for heat exchange. Of course, when increasing the scale, the heat capacity obtained decreases, because it involves different system boundaries. Thus, different studies of thermochemical materials are difficult to compare. Care also has to be taken when comparing this type of heat storage material with sensible or latent heat storage materials, for which the heat storage capacity is only linked to the material itself.

4.1. Sorption phenomena materials

4.1.1. Adsorption materials

Table 11 presents some micro (pore size <2 nm), meso (2 nm $<$ pore size <50 nm) and macroporous (pore size >50 nm) materials such as silica gel, alumina-phosphates, silico-aluminophosphates and zeolites, which have been widely investigated and characterized in recent years [142,143]. These compounds are the most widespread sorbents for water vapor adsorption. Their sorption behavior is based on the presence of regular or irregular pore systems within their molecular structure. A relation between the pore size and sorption capacity of these materials has been introduced over the past few years [144,145]. The molecular polarity of these substances also influences their affinity for water.

Silica gels are widely studied as hydrophilic compounds due to their high affinity to water vapor, large water sorption capacity at low humidity, low cost, and easy regeneration (desorption completed at a sufficiently low temperature) [146,147]. Henninger et al. [148] present a review on the current developments on materials for solar heating and cooling heat storage processes. The authors argue that despite the good theoretical adsorption capacity of silica gel, according to the Dubinin theory [149], one disadvantage of the silica gel/H_2O pair is the low hydrophilic

Table 11
Sorbents materials for ad/absorption phenomena suitable for heat storage in buildings.

Phenomena	Class	Type	Characteristics	Water level sorption capacity (g/g*) and heat storage capacity	Characterization level	Ref
ADSORPTION	Mesoporous silicates	Silica gels	Pore dimension: from 2 nm for regular density to 15–20 nm for low density ones Pore volume: from 0.3–0.4 to 1.0–1.5 cm^3/g Surface area: 300–700 m^2/g Charge: >88 °C Discharge: 32 °C Commercially available and cheap	**0.40**: Silica gel type A, 2.2 nm pore size **0.45:** Silica gel type RD, 2.2 pore size HYDES Project: 450 MJ m^{-3} of silica gel MODESTORE Project: 180 MJ m^{-3} of silica gel	Material scale Reactor scale System scale	[240–244]
		Silica aerogels	Advantages: large surface, pore volume, open system of pores Drawbacks: instability of the molecular structure to moisture, low mechanical stability, low density	**1.35**: (100% SiO_2 with CO_2 supercritical drying) **1.25**: (100% Al_2O_3 with CO_2 supercritical drying) **1.15**: 70% SiO_2–30% Al_2O_3 with CO_2 supercritical drying	Material scale	[245]
		Ordered mesoporous silicates (MCM, SBA, etc.)	Advantages: mono-sized pores, high structure homogeneity, large pore surface and volume Drawbacks: Cylindrical or hexagonal pores	**0.83**: MCM-48, 2.8 nm pore diameter, 983 m^2/g surface area **0.81**: KIT-1, 2.9 nm pore diameter, 923 m^2/g surface area **0.44**: SBA-1, 2.1 nm pore diameter, 940 m^2/g surface area **0.84**: SBA-15, 5.0 nm pore diameter, 645 m^2/g surface area	Material scale	[246,247]
	Classical zeolites	Alumina-silicates	largest known class of crystalline porous solids: about 200 types Too high affinity to water at low ratio of Si/Al Charge: 130 °C Discharge: 65 °C	**0.20–0.45** Heat: 576 MJ/m^3 of zeolite 4A	Material scale Reactor scale	[240,243,248]
	Metal-aluminophosphates		Uniform pore size of 0.3 to 0.8 nm formed by 6–, 10–, 12 and 18-membered ring channels. Moderate affinity to water	**0.35**: VPI-5, ring size 18 **0.55**: SAPO-37, ring size 12 **0.14**: VAPO-5, ring size 12 **0.32–0.36**: GeAPO-5, MnAPO-5, ring size 12 **0.46**: SAPO-5, ring size 12 **0.46**: SAPO-40, ring size 12	Material scale	[249,250,251]
	Metal-organic frameworks		Regeneration at 45–50 °C Cold generation at 15 °C Low affinity to water		–	[245–247]
	Composite sorbents	Silicates + $CaCl_2$	Charge: 90 °C	**1.27**: $CaCl_2/SiO_2$aerogel (29% $CaCl_2$) **1.17**: $CaCl_2/SiO_2$ xerogel (28.6% $CaCl_2$) **0.80**: $CaCl_2$/silica gel (with 33.7% $CaCl_2$) **0.60**: $CaCl_2$/silica gel (with 24% $CaCl_2$) Heat: 806 MJ/m^3	Material scale –	[169,183,252,253]
		Silicates + LiBr	–	**0.80**: Libr/SiO_2 aerogel (28.6% LiBr), pore size 7.5 **0.76**: Libr/densified SiO_2 aerogel (28.6% LiBr), pore size 12.9	Material scale	[252,254,255]
		Zeolite 13X + $MgSO_4$	Charge: 150 °C Discharge: 30–50 °C	597.6 MJ/m^3 (15%wt $MgSO_4$) 640.8 MJ/m^3 (10%wt $MgSO_4$)	Material scale	[158,256]
		Expanded natural graphite + $SrBr_2$	Charge: 70–80 °C Discharge: 35 °C (heating), 18 °C (cooling)	Heat: 216 MJ/m^3 of reactor Cooling: 144 MJ/m^3 of reactor Power: 2.5 kW (heating); 4 kW (cooling)	Reactor scale	[184]
			Charge: 62–65 °C		Reactor scale	[257]

Table 11 (*continued*)

Phenomena	Class	Type	Characteristics	Water level sorption capacity (g/g*) and heat storage capacity	Characterization level	Ref
		Expanded vermiculite+$LiNO_3$	Discharge: 33–36 °C	**0.4**H_2O/g of composite material Heat: 450 MJ/m^3 of reactor		
ABSORPTION	Salts	$NaOH/H_2O$	Charge: 100–150 °C Discharge: 40–65 °C	Heat: 900 MJ/m^3 of NaOH (with single stage reactor).	Reactor scale	[161,258]
		$LiCl/H_2O$	Charge: 46–87 °C Discharge: 30 °C	Heat: 910.8 MJ/m^3 of LiCl (with crystallization in the storage tank)	Reactor scale	[128,240,259]
		$CaCl_2/H_2O$	Charge: 70–80 °C Discharge: 21 °C	Heat storage: 428 MJ/m^3 of solution	Reactor scale	[165,260]
		$LiBr/H_2O$	Charge: 40–90 °C Discharge: 30–33 °C	Heat storage capacity: 907.2 MJ/m^3 of solution	Reactor scale	[164]

(–): not available.

* Measurements were performed at 25 °C and P/P_0=1.0.

characteristic within the working window consisting of adsorption at 35 °C and 1.2 kPa and desorption at 150 °C and 5.6 kPa.

Silica aerogels by definition are hydrophilic and extremely porous amorphous silica materials consisting of aggregated SiO_2 networks [150]. The aggregated porous structure improves the water uptake behavior of these materials (> 1 g/g, Table 11) in comparison to silica gel (< 0.5 g/g). Silica aerogels are commonly used as thermal insulators, catalyst supports, dielectric materials and sorbents for organics or water vapors [151,152]. However, unlike silica gels, silica aerogels face difficulties in their use as thermochemical materials because of the collapse of their molecular structure (Si–O–Si) during their exposure to moisture [153].

Zeolites are hydrophilic sorbents given their electrostatically charged framework. They are usually used as desiccants based on their high concentration of active sites, which enhances the water uptake capacity. In the literature, the most commonly studied zeolites for solar-assisted energy storage in buildings are faujasites (FAU framework) and zeolites type A (LTA framework), and the temperature increase during the adsorption phase can be averaged at 23 °C depending on the system's configurations [149,154–157]. In [148], zeolites are presented as more hydrophilic than silica gel but with a major disadvantage concerning solar-assisted applications: their desorption temperature is higher than 200 °C for a maximum regeneration of the material. This is due to the strong interaction between their electrostatically charged framework and the water molecules. However, in practice, some experiments showed that good results can be achieved with a desorption temperature of 120 °C [158]. In Mintova et al. [150] and Henninger et al. [148], a study on the reduction of the strongly hydrophilic character of zeolite is presented. The authors argue that solutions such as the variation of the Si/Al ratio or the dealumination showed promising results. Another study from Henninger et al. [155] reported the influence of the type of cation on zeolite water uptake with a new fingerprinting method. Different types of zeolite with different types of cations were investigated: Na-A, Li-A, Li-LSX (low silica X, Si/Al ratio=1), Pb-Y, Ni-Y, Na-Y, Li-Y, LaNa-Y. The tests showed that for the type A and the faujasite framework type (X and Y zeolites), the lithium exchanged form (Li-A, Li-LSX, Li-Y, LaNa-Y) had the most promising performance (43 g/kg of active material for Li-Y, 24 g/kg of active material for Li-LSX) for a low heat driving temperature (< 95 °C). With a much higher desorption temperature of 140 °C, the water uptake was also significantly improved (by a factor of 7).

Another class of sorbents, aluminophosphates ($AlPO_4$) and silica-aluminophosphates (SAPO-34) were intensively studied for use in adsorption processes for heat storage purposes. These materials present a similar molecular framework and pore configuration to zeolites and are often called "zeolite-like" materials. In Janchen et al. [143,156], a study on the water sorption capacity is presented. The authors found that $AlPO_4$ and SAPO-34 molecular sieves have similar water adsorption value as zeolite, with the significant advantage of a lower desorption temperature. Henninger et al.[155] conducted investigations on the water adsorption characteristics of three samples of AlPO-18 and SAPO-34 as novel materials for heat storage applications. The authors found that for a desorption temperature of 95 °C, AlPO samples (resp. SAPO samples) had a water uptake of 253 g/kg of material (resp. 200 g/kg of material), which is more than six times (resp. five times) higher than the value of silica gel used as the reference material for these tests. Performances were improved of 20% for a desorption temperature of 140 °C. With regard to their hydrophilic behavior, $AlPO_4$ and SAPO-34 can be very promising candidates for adsorption processes in buildings, although their actual high synthesis cost limits the massive use of these materials [143,148].

A novel class of microporous materials namely metal-organic framework (MOFs) has recently been investigated for adsorption application purposes [154,157]. Like zeolites and $AlPO_4$, MOFs are crystalline open porous materials with a one, two or three-dimensional framework [148]. In terms of their internal pore surface area and volume, these materials present good water uptake potential and they have recently been characterized [148,154,157,159].

For thermochemical energy storage units, the choice of the storage material is critical. A perfect match of the material's properties with the cycle working conditions could allow significant improvements in the system's performances. According to Gordeeva et al.[141], the common way to select the best adsorbent for a given application is to screen the properties of available adsorbents in order to choose which the best meets the application demands. The author argued that this method is difficult and time-consuming and usually results in a compromise choice rather than the ultimate one. One promising and more precise method namely the target-oriented design is proposed in [160]. Gordeeva et al.[141] describes it as follow: (1) determining the demand (based on thermodynamic analysis of the cycle efficiency) of the application for the required storage material properties, (2) choice of the candidate material (based on equilibrium sorbent-sorbate), whose properties precisely or nearly fit these demands.

4.1.2. Absorption materials

Throughout the literature, the most frequently studied pairs for absorption heat storage are $NaOH/H_2O$, $LiCl/H_2O$, $LiBr/H_2O$ and $CaCl_2/H_2O$, as shown in Table 11.

In [161], a closed sorption thermochemical heat storage system is studied, using sodium hydroxide (NaOH) as the reactive sorbent. The single-stage prototype consists of three storage tanks, a processing unit with integrated heat exchangers, pumps, and connections to the cold and hot water supply. The system is designed in a modular way. Experimental tests with a 160 kg sample of NaOH combined with the same amount of water provided 8.9 kWh of heat with a power of 1 kW. The energy density of the material deduced from these results amounts to 900 MJ/m^3 of solution. A low level heat input at 150 °C was needed to completely charge the system. Analyses show that the concentration ratio of the salt, the corresponding vapor pressure, and the temperature of the discharge are significant parameters. The heat storage capacity of the system is limited by a high temperature needed during the discharge phase. This can be overcome, according to the author, with the implementation of a double-stage system [118,161]. But, compared to single-stage cycles, the charging efficiency (ratio of heat stored on heat input) of double-stage cycles decreases due to the lower supply temperature and the increased number of transfer processes.

Hydration and dehydration of lithium chloride were tested and projected sizes of heat storage densities for hypothetical stores with 252 MJ (short-term) and 3600 MJ (long-term) storage for single family homes were evaluated in a thermochemical accumulator (TCA) [162]. A TCA is an absorption process that uses the $LiCl/H_2O$ working pair in the liquid, vapor and solid (sorbent) phase [162,163]. Results from laboratory tests showed that the energy storage for a prototype containing 54 kg of LiCl is approximately 126 MJ for heating, and 80 MJ for cooling [162], corresponding to an energy storage density of 910 MJ/m^3 of material under these conditions. The authors argue that the system's energy storage density could have been increased if the solution was used over a larger concentration range. The concept is still under development and will need to remedy several limitations to its widespread use such as the high cost of the LiCl.

Dynamic simulations on the heat storage capacity of the $LiBr/H_2O$ pair have been conducted for a 120 m^2 single-family dwelling that meets Passive House standards in Chambéry, France [164]. A prototype was also designed and tested. Simulations depicted that the system presents a heat storage capacity of 907 MJ/m^3 of LiBr aqueous solution for a mean heat supply temperature of 30 °C. During the experimental tests, the mass fraction of LiBr varied within the 50–67 m% range. Crystallization is presented as a phenomenon that can increase the storage density of the system by more than a factor of 3. However, it can induce constraints such as circulation difficulties within the machine. The system also exhibits better performance (increased storage density) when reducing the heat supply temperature.

The storage capacity and the influence of several factors such as the operating pressure and the temperature needs, the presence of the air in the generator, etc. on the performance of a system using $CaCl_2/H_2O$ was studied in [165]. A prototype was also set up and tested. Dynamic annual simulations were performed and the power obtained during the desorption phase was 0.6–4 kW [165]. The storage capacity of the $CaCl_2/H_2O$ combination obtained is about 418 MJ/m^3 of solution and the efficiency of the system about 66.4% [165].

4.2. Chemical reaction materials

4.2.1. Pure thermochemical materials

For chemical heat storage reactions, hygroscopic salts such as calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), aluminum sulfate (Al_2SO_4), and magnesium sulfate ($MgSO_4$), show good potential and can lead to significant amounts of heat stored (resp. released) (Table 12) [166–169]. Chemical reaction materials present higher heat capacities than sorption materials.

Azpiazu et al.[170] performed a heat recovery experience from a thermal energy storage based on the $Ca(OH)_2/CaO$ cycle. Dehydration and hydration cycles of the material were studied. Two samples of 5 and 8 g of CaO were tested. Dehydrations tests of $Ca(OH)_2$ were performed inside a furnace at 550 °C during 45 min with a 10 °C/min rate. Results showed weight losses of 18% for 5 g samples and 20% for 8 g samples. Compared with the stoichiometric loss of 24%, this indicates a non-complete desorption reaction which in return can cause irreversibility after several cycles. During hydration tests, CaO was first cooled down at 0 °C and water at 0 °C was added to the material at a proportion of 1/1.5 (i.e. 7.5 ml for 5 g samples and 12 ml for 8 g samples). In this case, the heat generated by the exothermic reaction is partially used to heat CaO and water up to 25 °C. The heat recovering device consisted of 15 ml for 5 g samples and 24 ml for 8 g samples of an aqueous antifreeze solution at 0 °C surrounding the setup. Results showed that for the two samples, the antifreeze solution always reached an approximated final temperature of 35 °C which remained basically constant for few minutes. The author explained that this occurs because the solution is still receiving heat from the reacting bed, at a lower heat transfer rate because of the low temperature gradient at this step. One solution to recover more heat can consist in changing periodically the heat recovery solution.

Some problems are usually encountered during the hydration process of the above-mentioned salts. Bringing the water vapor into contact with the salt is sometimes difficult to achieve. A skin of the hydrated salt forms on the surface of the bulk powder and greatly limits the diffusivity of the water vapor within the unreacted part of the sorbent. To improve heat and mass transfer within the reactive bed, porous hosts have been developed over the past two decades. They combine the heat storage capacity of the salt and the heat storage capacity of the host (in porous sorbent materials such as silica gel and zeolites), or in addition to the good heat and mass transfer performance of the host (in nonreactive host materials, such as expanded natural graphite [126,134,171–174], metal foam [175], carbon fiber [176,177] or activated carbon [178]). The use of composite materials as well as the reactor design has been found to considerably improve the heat and mass transfer within thermochemical processes [132–134,138,141]. Moreover, according to Gordeeva et al.[141], the use of a host matrix strongly affects the sorption equilibrium of the salt with the sorbate. For the composite $Ca(NO_3)_2$/mesoporous silica, the author presented the isobars of water sorption as a linear combination of the sorption isobars of the salt and the matrix, taken with proper weight coefficients correspondent to their relative content. Another study on the influence of the host material on the water sorption properties of the composite $CaCl_2$/SBA-15 is reviewed in [141,179]. The author concluded that inside silica mesopores of 8–15 nm, the salt absorbs water identically to the bulk solution. But inside narrower pores of 3–8 nm, its sorption ability decreases compared with the bulk material [180].

4.2.2. Composite thermochemical materials

In general, for heat storage applications, composite materials are defined as the combination of a salt hydrated and a host with a porous structure and high thermal conductivity [169,181]. The methods usually used to produce composite materials are simple mixture, impregnation, or a mixture/impregnation and consolidation [182]. For all these methods, the procedure usually consists of 4 steps: (1) a preliminary drying of the host material to remove adsorbed water, (2) an impregnation of the host material with the salt solution, (3) a filtration of the mixture and (4) a final drying of the wet composite. In Gordeeva et al.[141], a detailed description

Table 12
Material couples suitable for chemical heat storage in residential applications.

Material/Couple	Operating Conditions	Performances	Characterization level	References
$M_gSO_4 \cdot 7H_2O \rightarrow MgSO_4 + 7H_2O$	Charge: 122–150 °C Discharge : 122°C	Heat:1512 MJ/m^3 of M_gSO_4 (theoretical). Hard recovery	material scale ECN project: Characterization of the material (experimental tests) sample of 10 mg of material	[166,240,261–263]
$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 2H_2O + 4H_2O$	Charge: 115–130 °C Discharge: 35 °C	Heat: 2170.8 MJ/m^3 of $MgCl_2 \cdot 2H_2O$	Material scale IEC Project: material characterization. Sample of 250 mg of material. Stabilization with zeolite 4A to be further considered.	[264]
$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot H_2O + 5H_2O$	Charge: 150 °C Discharge: 30–50 °C	–	Material scale ECN project: material characterization Sample of 300 g of material.	[167]
$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2O + 4H_2O$	Discharge: 40–60 °C (heat supply at ≥ 40 °C to ignite discharge)	Heat: 2066.4 MJ/m^3 of $CuSO_4 \cdot H_2O$ (theoretical)	ITW project: characterization of 100 mg of material	[265]
$CaCl_2 \cdot 2.3H_2O \rightarrow CaCl_2 + 2.3H_2O$	Charge: 150 °C Discharge (temperature lift): $\Delta T = 62$ °C (reactor and evaporator both at 25 °C) $\Delta T = 10$ °C (reactor at 50 °C and evaporator at 10 °C)	–	ECN project:sample of 40 g of material.	[166,261]
Bentonite + $CaCl_2$	Discharge: 35 °C	Heat: 667 MJ/m^3 of composite material	ITW Project: Material characterization	[266]
$KAl(SO_4)_2 \cdot 12H_2O \rightarrow KAl(SO_4)_2 \cdot 3H_2O + 9H_2O$	Charge: 65 °C Discharge: 25 °C	Heat: 864 MJ/m^3 of $KAl(SO_4)_2 \cdot 3H_2O$	Reactor scale PROMES CEA-INES Project: prototype of 25 kg of $KAl(SO_4)_2 \cdot 12H_2O$	[267]
$Al_2(SO_4)_3 \cdot 18H_2O \rightarrow Al_2(SO_4)_3 \cdot 5H_2O + 13H_2O$	Charge: 150 °C Discharge (temperature lift): $\Delta T = 9.8$ °C (reactor and evaporator both at 25 °C) $\Delta T \sim 1$ °C (reactor at 50 °C and evaporator at 10 °C)	–	Reactor scale. ECN Project: Sample of 40 g of material	[166,261]
$Na_2S \cdot 5H_2O \rightarrow Na_2S \cdot 1.5H_2O + 4.5H_2O$	Charge: 83 °C Discharge: 35 °C	Heat: 2808 MJ/m^{3}of $Na_2S \cdot 5H_2O$ cold: 1836 MJ/m^3 of $Na_2S \cdot 5H_2O$	Reactor scale ECN project: SWEAT prototype, 3 kg of material Short-term heat and cold storage	[112]
$SrBr_2 \cdot 6H_2O \rightarrow SrBr_2 \cdot H_2O + 5H_2O$	Charge: 70–80 °C Discharge: 35 °C	Heat: 216 MJ/m^3 of $SrBr_2 \cdot H_2O$ possible cold recovery at 18 °C	Reactor scale PROMES CEA-INES Project: SOLUX prototype,170 kg of $SrBr_2 \cdot H_2O$	[184,268]
$CaCl_2 \cdot 2H_2O \rightarrow CaCl_2 \cdot H_2O + H_2O$	Charge: 95 °C Discharge: 35 °C	Heat: 720 MJ/m^3 of $CaCl_2$	Reactor scale BEMS: theoretical study	[269]

(–): not available.

of step 2 which can be performed through 2 different pathways is presented: the dry impregnation method (when the volume of the salt solution equals the pore volume of the matrix) and the wet impregnation method (when the matrix grains are immersed into the salt solution, which volume exceeds the pore volume of the matrix). The authors argue that since the filtration step is omitted for the dry impregnation method, it is easier in realization but special procedure and equipment are required for large amount of composite materials preparation to ensure a uniform distribution of the salt solution through the matrix.

Hongois et al.[158] developed a chemical heat storage system based on the hydration and dehydration of the composite material zeolite/$MgSO_4$ for seasonal heat storage in buildings. $MgSO_4$ was dispersed inside zeolite 13 X to enhance the reaction kinetics by providing a larger exchange surface and therefore improve the heat and mass transfer within the reactor bed. The system is intended to recover moisture from the ventilation exhaust air of the building as a source of water for the exothermal hydration reaction. With an airflow rate of 8 L/min and inlet air at 50% of relative humidity, tests conducted on 10 mg of composite material showed a 30 °C temperature increase, whereas it was 16 °C (resp. 23 °C) for the pure silica gel (resp. zeolite 13X) tested under the same experimental conditions.

Zhu et al.[183] studied a composite sorbent of mesoporous silica gel impregnated with calcium chloride, dedicated to low level heat storage. As a result, the water sorption measurements at 30 °C and a relative vapor pressure of 0.8 showed that the maximum adsorbed amount of water, 0.73 g/g of composite, was 4.87 times higher than that of silica gel (0.15 g/g of silica gel) under the same experimental conditions. During discharge, the temperature of the system varied from 30 °C to 45 °C and the system was fully recharged below 90 °C. Under the same conditions, the thermal energy storage tests on a macroscale setup filled with 40 kg of composite sorbent pellets showed a heat storage capacity of approximately 1 kJ/g.

A solid–gas sorption process with the bromide strontium/water ($SrBr_2 \cdot 6H_2O$) couple, combined with a solar thermal system was developed by Mauran et al.[184] for floor heating and cooling. The reactive substance ($SrBr_2$) was dispersed in a graphite matrix (expanded natural graphite). As a result, the system developed a storage capacity of 216 MJ (resp. 144 MJ)

for heating (resp. cooling) with a charging temperature as low as 70–80 °C and a discharge temperature of 35 °C (resp. 18 °C). However, according to the authors, the power delivered by the system was lower than expected (2.5–4 kW). One cause is the low value of the heat transfer coefficient (5–30 W/(m^2 K)) at the interface between the reactive layer and the heat exchanger wall.

More tests under different experimental conditions (such as an open system) on $MgCl_2$ were conducted by Zondag et al.[185]. The choice of an open system was made by the authors based on the results of a technical-economical study conducted by Zondag et al.[186], which indicated that this reactor type was most promising in terms of economics and reliability. A carrier material (cellulose) was used to avoid problems related to overhydration such as the formation at the top of the bed of a solid layer, resulting in an increase in the pressure drop over the bed. Also, a maximum temperature of 130 °C was set to limit the formation of hydrogen chloride vapor during desorption. The results from tests of the hydration of 245 g of $MgCl_2$ showed a 20 °C temperature increase, which is a promising result for the use of this material for seasonal domestic heat storage for space or water heating.

Others experiments on composite materials were conducted by Janchen et al.[142,156] on zeolites (granulated zeolite CaNaA-60, LiX–zeolite, MgNaX) and impregnated mesoporous materials (silica/$CaCl_2$, aluminosilicate/30%$CaCl_2$). A comparative analysis on the water sorption capacity and the thermochemical heat storage capacity was carried out between zeolite and the impregnated mesoporous materials. As a result, heat resulting from sorption of the zeolites was significantly higher than that of the impregnated mesoporous materials, but the water uptake of the latter (0.28 g/g) was clearly higher than in zeolites (0.17 g/g).

5. Conclusion

This paper presents a review of the current energy storage materials developed and used in buildings heat storage systems. Water remains the most widely used material in sensible heat storage systems. It is the material that presents the best compromise between cost, heat storage capacity, density, and environmental impact. Most of the technological projects are today focusing on the development of tools for the optimization of residential energy consumption more than on the development of new systems with water for energy storage management. However, there has been a breakthrough in the use of packed beds and the building structure for heat storage. A number of research studies, both numerical and experimental, were carried out on packed beds to investigate the effects of various parameters such as the shape and size of the packing materials and the void fraction on the system's performance.

Considering latent heat storage, numerous PCMs have been developed for the 0–80 °C temperature range, which is suitable for building heating needs. The advantages of latent heat storage materials on sensible heat storage materials is well established with their high storage energy density and the various melting temperatures that allow different levels of use. The investigations on these materials are still underway and are attempting to overcome a number of their limitations (low thermal conductivities, supercooling, incongruent melting, etc.) and improve their viability. Research on heat transfer enhancement techniques using fins and encapsulations is currently underway. Also, some of the research work is focusing on the integration of these materials into the building's structure, a real challenge for building energy storage applications. However, even though numerous studies are available on these materials, some of their thermophysical properties (thermal conductivity, specific heat, density) have not yet been fully assessed.

Considering thermochemical heat storage, the technique theoretically offers the greatest heat storage capacity and does not suffer from heat losses during the storage period. But the literature on these materials is marginal compared to sensible and latent heat storage materials. The reason is that the research in this field is still in an early stage. Among the pairs of materials that have been listed, silica gel/water, magnesium sulfate/water, lithium bromide/water, lithium chloride/water, and sodium hydroxide/water appear to be at the most advanced stage of research. There has been an intensification of the research during the last decade to develop more efficient adsorption heat storage systems. The use of carrier materials with a high porous structure with a reactive material dispersed inside to improve the heat and mass transfers is one major direction of this research activity. New thermochemical materials have been characterized and innovative system designs have been developed and tested. However, more than these necessary improvements, future research work should focus on the perfect integration of these technologies into the building systems and also on the development of standard testing procedures to determine the thermophysical properties of materials. Indeed, the measurement method and test scale have a large influence on the properties measured and consequently greatly impacts the design of storage systems. Within the IEA SHC Task 42/24 [187], several research institutes are, among others, focusing on how to introduce measurement-standards dedicated to energy storage materials.

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